

Synthesis and Evaluation of 1,3a,6a-triazapentalene (TAP)-bonded system

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Abstract: A method of synthesizing a directly connected 1,3a,6a-triazapentalene (TAP) ring system as a linearly bonded aromatic system with a planar form was established. Various TAP-dimers and a 2-alkyl-TAP-trimer were synthesized and their fluorescence properties were evaluated. Although the direct connection of the TAP ring with other TAP rings did not affect the fluorescence properties in diluted solvent, TAP-dimers showed unique fluorescence properties derived from the aggregation state under highly concentrated conditions. In particular, TAP-dimer **5f** showed aggregation-induced emission in highly concentrated solution, and **5b** showed typical mechanochromic fluorescence in the solid state despite their compact molecular size.

Introduction

Linearly bonded aromatic systems as rigid polyarene wires have received a great deal of attention by virtue of their interesting functions such as their conductive properties, high fluorescence, and molecular aggregation.^[1,2] However, almost all polyarenes have a twisted form due to the steric repulsion of hydrogens at the ortho position, and in many cases the expected functions cannot be fully demonstrated. Therefore, the introduction of various bridges into adjacent aromatic rings for the retention of the planar form have been intensively studied.^[3] On the other hand, we have recently developed 1,3a,6a-triazapentalene (TAP) as a novel fluorescent chromophore that possesses a 10 π -electron system in its compact bicyclo[3.3.0]octane skeleton.^[4] This aromatic framework, in which five-membered rings are condensed with each other, is expected to linearly connect to other TAP rings, and the steric repulsion of the ortho hydrogen is

reduced due to the sharp angle of each five-membered ring, so that the TAP-bonded system would keep a planar form (Fig. 1).^{[4],[5]} In addition, since TAP has a specific dipole structure within its aromatic skeleton, the connection of TAP would provide a novel wirelike molecule with an alternating charge. Therefore, the TAP-bonded system characterized by a linear connection, a planar form, and an alternating charge was expected to form a unique aggregation state with a drastic change in fluorescence properties. Here we report the first synthesis of a TAP-bonded system and the evaluation of its fluorescence properties with changes in aggregation states.

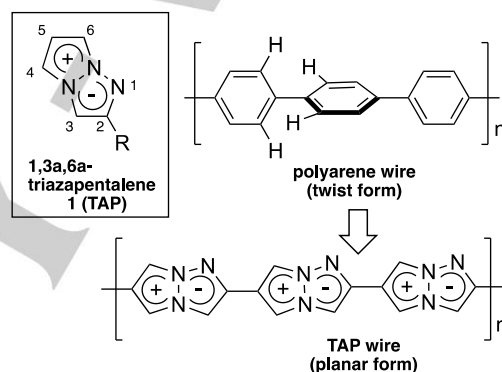


Figure 1. TAP wire

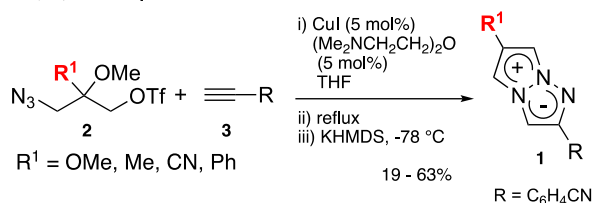
We have recently developed various TAP derivatives as compact fluorescence reagents^[6] and elucidated the substituent effects of a TAP system.^[7] During our investigation of the substituent effects, we established a method of synthesizing a 2,5-disubstituted-TAP analog and found a 5-substituent to be useful as a regulator of the fluorescence intensity of TAP.^[8] The 2,5-disubstituted-TAPs were synthesized by one-pot reactions of i) click reactions of alkynes **3** with azidotriylates **2**,^[9] ii) cyclization of the resulting triazole, and iii) elimination of the methoxy group followed by aromatization (Fig. 2a). Thus, when 5-ethynyl-TAP analog **4** was synthesized by a similar sequential reaction of **2a** (R^1 = ethynyl), we considered that the 5-ethynyl group of TAP **4** could be used in the next similar sequential reaction to give TAP-dimer **5**. Since this resulting TAP-dimer **5** also has the ethynyl group at the 5-position, further similar sequential operation would afford TAP-trimer **6**. Then, the TAP-bonded system would be sequentially extended by repeating the same procedure (Fig. 2b).

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a) Previous synthesis of 2,5-disubstituted-1,3a,6a-triazapentalene



b) TAP wire synthesis

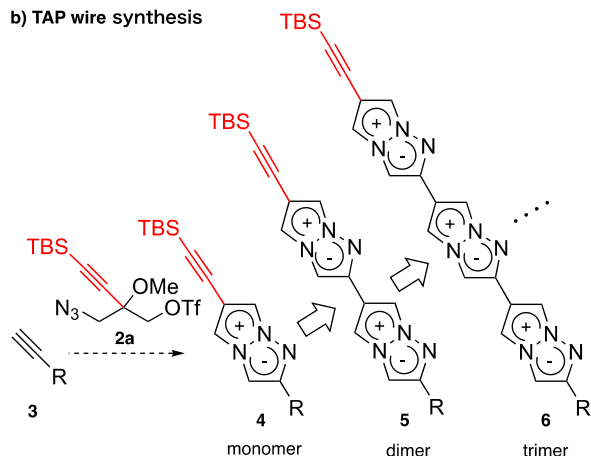
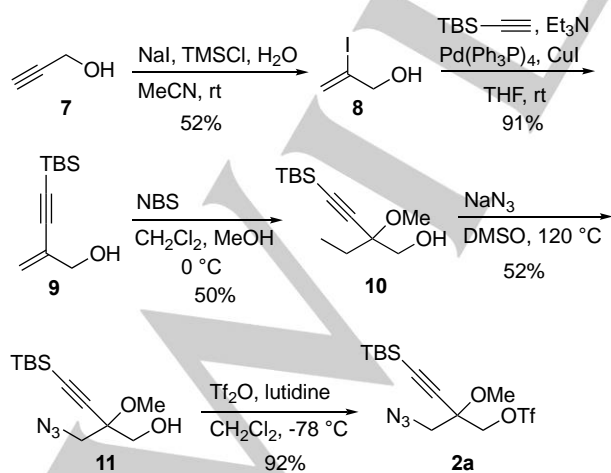


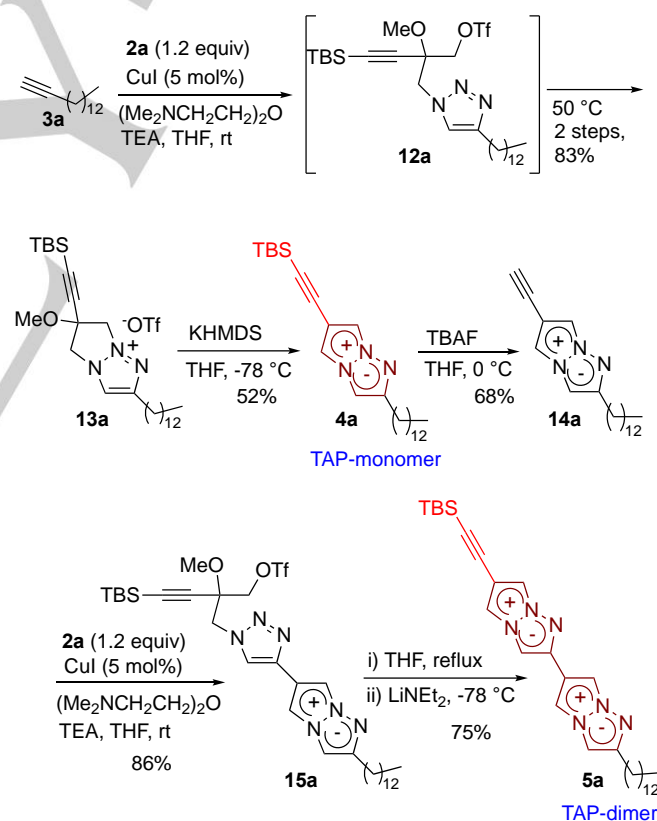
Figure 2. Synthetic plan for TAP wire

Results and Discussion

First, we started the synthesis of azide unit **2a**. Treatment of propargyl alcohol **7** with NaI and TMSCl in the presence of 1.2 equiv of H_2O afforded vinyl iodide **8** in 52% yield.^[10] The Sonogashira coupling of **8** with (*tert*-butyldimethylsilyl)acetylene gave an enyne **9** in good yield,^[11] and the subsequent bromo etherification of **9** by treatment with NBS in dichloromethane including methanol afforded **10** in 50% yield. Finally, **10** was converted into the desired azidotriflate **2a** by the sequential operation of azide and triflate formation (Scheme 1).

Scheme 1. Synthesis of azide unit **2a**

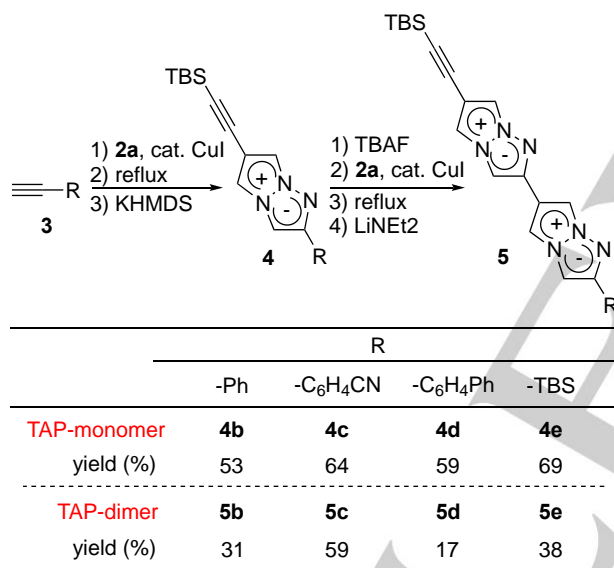
Having prepared azide unit **2a**, we examined the synthesis of 5-ethynyl analog from pentadecyne **3a** in order to increase the solubility of the TAP-bonded system in organic solvent. The click reaction of **3a** with **2a** afforded triazole **12a** smoothly, and the reaction mixture was heated directly to 50 °C to give bicyclic intermediate **13a** in 83% yield from **3a**. Treatment of **13a** with KHMDS in THF at -78 °C afforded the desired TAP-monomer **4a** in 52% yield. It should be noted that the direct treatment of **13a** with KHMDS in one pot from **12a** showed a decline in yield. With 5-ethynyl-TAP **4a** in hand, we attempted to synthesize the TAP-dimer. After removal of the TBS group, the resulting **14a** was treated with **2a** in the presence of copper(I) catalyst to give **15a** in 86% yield. Since a bicyclic intermediate derived from the cyclization of **15a** was readily decomposed during column chromatography, unlike the result of TAP-monomer synthesis, **15a** was purified at this stage to induce the next sequential reaction reproducibly. That is, after the cyclization of purified **15a** under THF reflux condition, the mixture was cooled to -78 °C and treated directly with LiNEt_2 to afford the desired TAP-dimer **5a** in a 75% two-step yield. In the case of the second TAP formation, the reaction using KHMDS as the base did not proceed; a stronger base was needed.

Scheme 2. Synthesis of TAP-dimer **5a**

Having established a method of synthesizing TAP-dimer **5a**, we synthesized various TAP-dimers possessing other substituents at the 2-position (Scheme 3), because the

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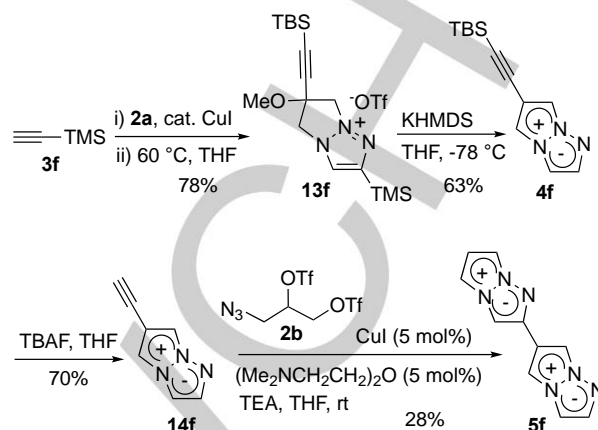
fluorescence wavelengths and intensities of the TAP derivative change widely depending on the 2-substituent.^[4] The similar sequential operations of phenylacetylene (**3b**) and (4-cyanophenyl)acetylene (**3c**) afforded TAP-monomers **4b** and **4c** in 53% and 64% yields, respectively, and then **4b** and **4c** were also similarly converted to TAP-dimer **5b** and **5c** in 31% and 59% yields, respectively. On the other hand, although TAP-monomer **4d** was obtained from (biphenyl)acetylene (**3d**) without a significant decrease in yield, the formation of TAP-dimer **5d** showed a considerable decline in yield (17%). Whereas the TAP-dimer forming reaction proceeded smoothly, the main reason for the low yield was that the purification of **5d** was difficult due to its poor solubility in solvents. Furthermore, the reaction of (*tert*-butyldimethylsilyl)acetylene (**3e**) also proceeded smoothly to afford TAP-monomer **4e** in 69% yield. Although **4e** possesses two TBS groups, treatment with TBAF removed only the TBS group on acetylene. A subsequent similar operation gave TAP-dimer **5e** possessing the TBS group at the 2-position. Thus, this method was shown to be applicable to the synthesis of various TAP-dimers.



Scheme 3. Synthesis of various TAP-dimers.

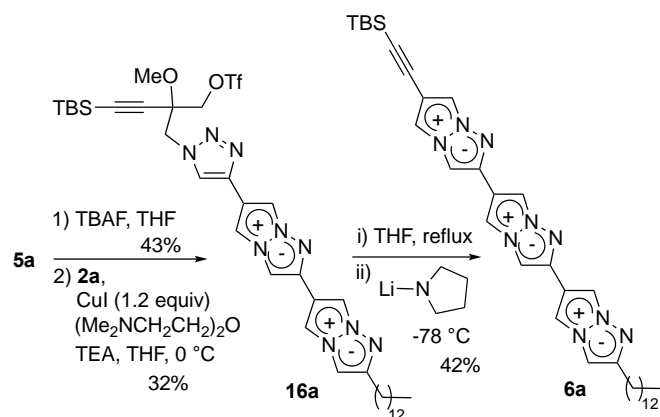
Next, we tried to synthesize the unsubstituted TAP-dimer to elucidate the natural properties of the TAP-dimer skeleton. Since the TBS groups of **4e** and **5e** on the TAP ring could not be removed despite various efforts, we started the TAP-dimer synthesis from (trimethylsilyl)acetylene **3f**. The click reaction of **3f** with **2a** afforded the expected triazole, followed by direct heating of the mixture at 60 °C to give bicyclic intermediate **13f** in 78% yield. Following this procedure, **13f** was treated with KHMDS to form 5-ethynyl-TAP, yielding **4f** (63%) with the simultaneous removal of the TMS group. Subsequently, the TBS group on acetylene of **4f** was removed by treatment with TBAF to give primary acetylene **14f** in 70% yield. Finally, the TAP-ring-forming cascade reaction using azidoditriflate **2b**, which was previously

developed by our group, was applied to **4f**, and the desired unsubstituted TAP-dimer **5f** was first obtained.



Scheme 4. Synthesis of unsubstituted TAP-dimer **5f**.

Having established the preparation of TAP-dimers, we next tried to synthesize a TAP-trimer. After removal of the TBS group of TAP-dimer **5a** by treatment with TBAF, the resulting primary acetylene was applied to the 5-silylethynyl-TAP synthesis. However, the click reaction with **2a** in the presence of 5 mol% of copper(I) iodide did not proceed, and the desired triazole **16a** was not obtained at all. We considered that the TAP-dimer unit was strongly coordinated to the copper(I) catalyst and disturbed the reaction with primary acetylene. After various examinations, including appropriate copper ligand searches,^[12] we finally found that the use of a stoichiometric amount of copper iodide (1.2 equiv) at 0 °C afforded the desired **16a** in 32% yield. Next, although the cyclization of triazole proceeded readily under THF reflux condition, the subsequent elimination of the methoxy group did not occur by treatment with LiNEt₂, unlike the case with TAP-dimer formation. This is probably due to the fact that the acidity of the neighboring proton of the ammonium cation on the bicyclic intermediate was reduced by the delocalization of the cation charge with the elongation of the TAP bonded system. Actually, treatment with lithium pyrrolidide as the stronger base afforded the desired TAP-trimer **6a**. This is the first example of a TAP-bonded system. On the other hand, treatment of **5a** after deprotection of the TBS group with **2b** as the azide unit did not afford the TAP-trimer at all, even when an excess amount of **2b** was used. Thus, it is still difficult to synthesize an unsubstituted TAP-trimer. In addition, phenyl substituents (**5b-d**) could not be converted to TAP-trimers. Although the click reaction followed by cyclization of **5b** also proceeded, the elimination of the methoxy group by lithium pyrrolidide afforded decomposition. Meanwhile, the TBS substituent **5e** did not decompose in the elimination step, and the formation of TAP-trimer **6e** was observed along with the starting material (bicyclic triazolium ion). However, purification of **6e** was difficult due to the decomposition of the starting material and **6e** during column chromatography.



Scheme 5. Synthesis of TAP-trimer 6a.

After establishing these synthetic methods, we optimized the structures of TAP-dimer (5b) and TAP-trimer (6a) by density functional theory (DFT) calculation (Fig. 3 and supporting information). The most stable structure of trimer (6a) showed planar form with dihedral angles of 1.26° and -0.44° , respectively, along the C1-C2-C3-C4 and C1'-C2'-C3'-C4' bond of the two TAP moieties. The scan data for the rotation along these two C-C bond showed unstable high-energy structures when deviated from its planar form (supporting information).

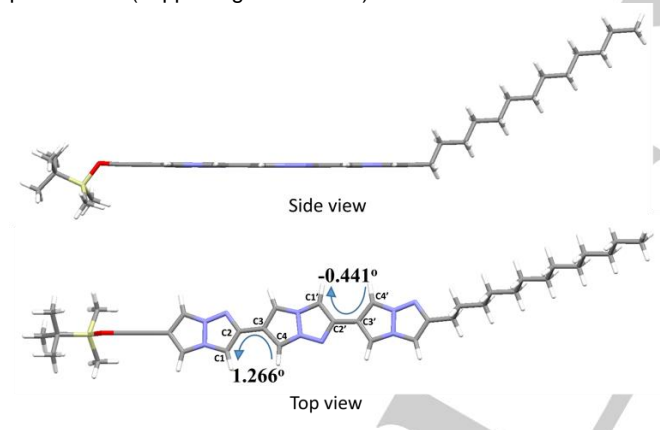


Figure 3. Optimized Structure of TAP-trimer 6a.

With the TAP-monomer (4a), -dimer (5a), and -trimer (6a) in hand, we next investigated the fluorescence properties of the TAP-bonded system in dichloromethane ($1.0 \times 10^{-6}\text{M}$). In comparison with TAP-monomer (4a), the fluorescence maximum of TAP-dimer (5a) showed a longer wavelength shift. However, TAP-trimer (6a) as an additional TAP bonded system showed a slightly longer wavelength shift from TAP-dimer (5a). Thus, further elongation of the TAP ring is predicted to hardly change the fluorescence wavelength. In addition, although the absorption maximum also showed a slightly longer shift in wavelength when the TAP rings increased, the effect was not strong. The fluorescence quantum yield (Φ_F) of 4a-6a also exhibited no tendency according to the extension of the TAP rings.^[13] On the

other hand, the molar absorbance coefficient (ϵ) greatly increased with the elongation of the TAP ring. It was therefore found that the direct connections and elongation of the TAP ring induce little change in the fluorescence properties with the exception of the ϵ in highly diluted dichloromethane solution.

Table 1. Fluorescence properties of TAP conjugate system.

	4a (n = 1) TAP-monomer	5a (n = 2) TAP-dimer	6a (n = 3) TAP-trimer
$\lambda_{\text{abs}}^{\text{max}}(\text{nm})$	322	343	350
$\lambda_{\text{em}}^{\text{max}}(\text{nm})$	461	503	505
Φ_F	0.012	0.002	0.007
$\epsilon (\text{dm}^3\text{mol}^{-1}\text{cm}^{-1})$	5926	7414	12317
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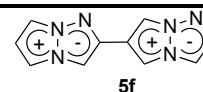
Table 2. Comparison of fluorescence properties between various TAP-dimers and TAP-monomers.

$$\text{TBS} \equiv \left[\begin{array}{c} \text{N}^+ \text{N}^- \\ \text{N}^+ \text{N}^- \end{array} \right]_n \text{R}$$

	R				
	-Ph	-C ₆ H ₄ CN	-C ₆ H ₄ Ph	-TBS	
TAP-monomer (n = 1)	4b	4c	4d	4e	1f
$\lambda_{\text{abs}}^{\text{max}}$ (nm)	342	389	354	332	-
$\lambda_{\text{em}}^{\text{max}}$ (nm)	411	497	448	487	389
Φ_{F}	0.070	0.42	0.27	0.007	0.017
ϵ (dm ³ mol ⁻¹ cm ⁻¹)	5828	3093	7800	5710	-
TAP-dimer (n = 2)	5b	5c	5d	5e	5f
$\lambda_{\text{abs}}^{\text{max}}$ (nm)	328	387	338	347	335
$\lambda_{\text{em}}^{\text{max}}$ (nm)	414	502	456	485	518
Φ_{F}	0.078	0.43	0.22	0.01	0.053
ϵ (dm ³ mol ⁻¹ cm ⁻¹)	12769	4438	12514	8430	2222

1f

5f



In addition to alkyl analog **4a-6a**, other TAP-dimers were also compared with TAP-monomers (Table 2). In the case of 2-phenyl analogs **5b-5d**, the fluorescence properties including fluorescence wavelength and intensities in diluted dichloromethane did not show a significant difference between TAP-monomers and TAP-dimers. On the other hand, a longer wavelength shift of the fluorescence maximum and an increase in the Φ_F were observed in the unsubstituted TAP-dimer **5f** in comparison with unsubstituted TAP ring **1f**. Throughout the comparison of various TAP-bonded systems including the 2-alkyl-TAPs, connection of the TAP ring was found to hardly induce any significant changes in fluorescence properties in the diluted solution, except for the unsubstituted TAP-bonded system.

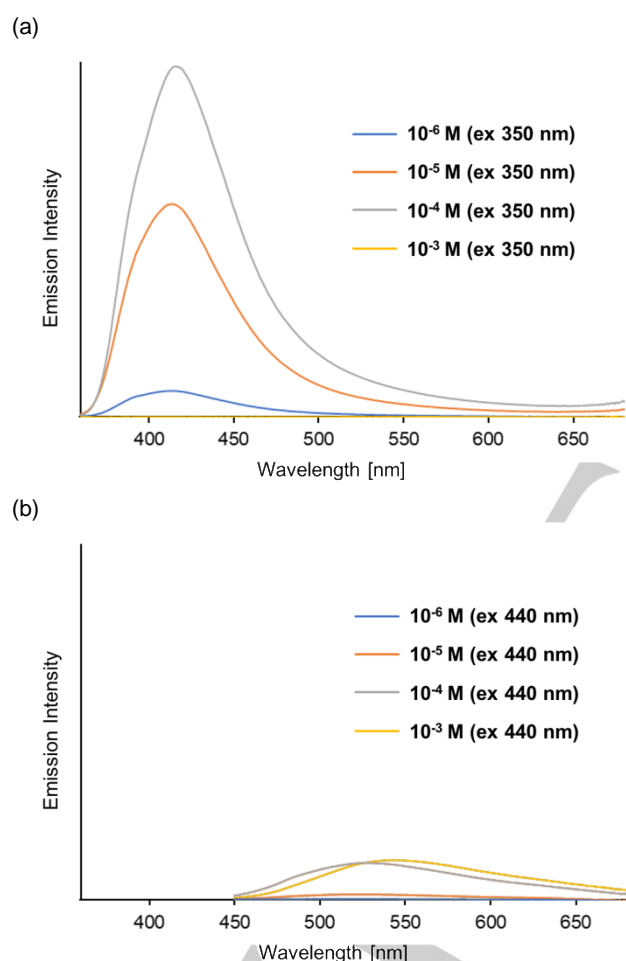


Figure 4. Fluorescence spectra of **5b** at various concentrations (10^{-6} to 10^{-3}), excited at (a) 330 nm and (b) 440 nm.

Although the TAP conjugate system showed no remarkable fluorescence properties in the diluted solution, the planar form of the aromatic TAP-bonded system is expected to readily aggregate intermolecularly with each other so that the intermolecular interaction in the concentrated state or in the solid state would induce interesting fluorescent properties. Thus, we

next investigated the concentration effect on fluorescence. The fluorescence intensity of TAP-dimer **5b** (excited at 350 nm) increased significantly in response to a rise in concentration from 1.0×10^{-6} M to 1.0×10^{-4} M, whereas further increases in concentration up to 1.0×10^{-3} M showed concentration quenching so that the fluorescence of **5b** disappeared (Fig. 4(a)).^[14] On the other hand, another fluorescence maximum (540 nm) was observed by the excitation at 440 nm in 1.0×10^{-3} M solution. This peak was not observed in the diluted solution (1.0×10^{-6} M) and increased with the rise in concentration (Fig. 4(b)). The results suggested that the TAP-dimer **5b** forms some intermolecular interaction in the concentrated solution.

In clear contrast to TAP-dimer **5b**, the fluorescence intensity of unsubstituted TAP-dimer **5f** was increased without concentration quenching by elevating the concentration (Fig. 5). A fluorescent dye that does not show concentration quenching is widely required for various functional materials such as luminescent dopants,^[15] and the elucidation of the underlying mechanism, including aggregation-induced emission,^[16,17] is underway in our laboratory.

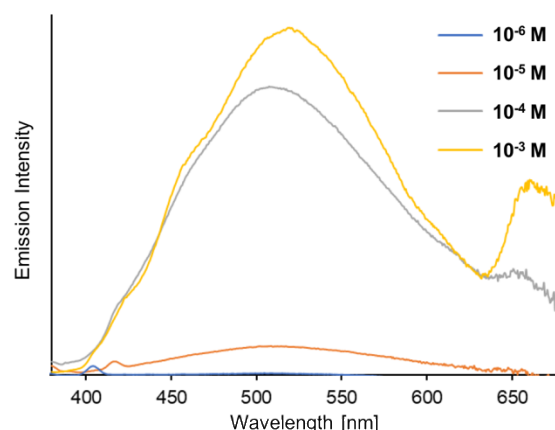


Figure 5. Fluorescence spectra of **5f** at various concentrations

In the bulk solid phase, the TAP-dimer **5b** shows a luminescent mechanochromism.^[18,19] A pristine sample of **5b** exhibits weak yellow-green emission under UV illumination. Hereafter, the as-prepared green-emitting solid sample of **5b** is called **5b-G** (Fig. 6a). By applying mechanical stimulation, the emission color of **5b-G** changes to a weak orange to give ground powder **5b-O** (Fig. 6a). This mechanochromic luminescence of **5b** is further evaluated by emission spectroscopy (Fig. 6b). **5b-G** exhibits a broad emission spectrum with a maximum at 535 nm (green line in Fig. 6b). Because of the low emission intensity (absolute emission quantum yield $\Phi_{em} < 0.01$), the spectrum does not show a good signal-to-noise ratio. The ground sample **5b-O** also shows a broad emission spectrum with a peak at 590 nm ($\Phi_{em} < 0.01$), confirming the 55-nm red shift upon grinding, as is typically observed for mechanochromic compounds. The distinct emission characteristics are also confirmed by the emission lifetime measurements of **5b-G** and **5b-O**, giving distinct decay curves with emission lifetimes of 4.9 and 1.2 ns, respectively (Fig.

S1). This experiment confirms the fluorescent character of **5b** even in the solid state.

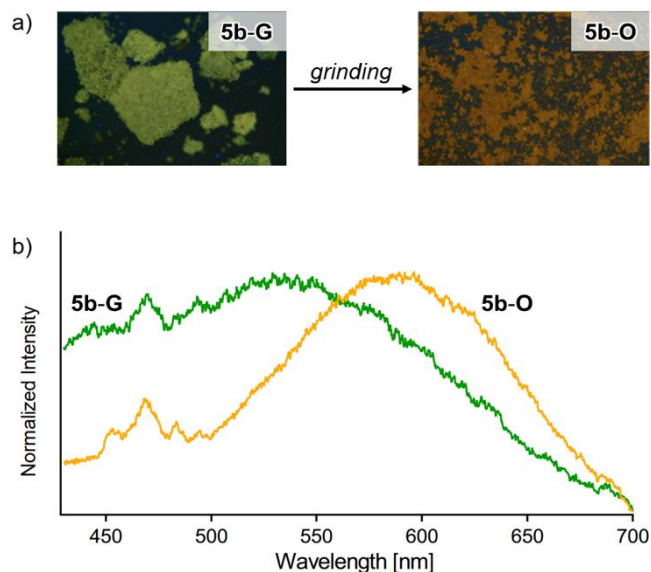


Figure 6. Photographs and emission spectra of **5b-G** and **5b-O** with the excitation at 365 nm.

To gain insight into the mechanism underlying mechanochromic fluorescence, powder X-ray diffraction studies of **5b** were performed (Fig. 7). Pristine **5b-G** shows several diffraction peaks, indicating a crystalline nature (green line in Fig. 7). After mechanical stimulation, **5b-O** shows almost no diffraction peaks (orange line in Fig. 7), indicating an amorphous form. This indicates that the luminescent mechanochromism of **5b** is based on the crystal-to-amorphous phase transition, as is typically observed for this type of material. This result, in light of the planar TAP skeleton and the observed red-shifted emission, implies that stacking interactions between TAP segments are strengthened upon amorphization in **5b-O**. Since the TAP-bonded molecular systems are a new class of luminophores, further optimization of the molecular structure might improve mechanofluorochromic performance, such as increasing fluorescent intensity and extending emission wavelength.

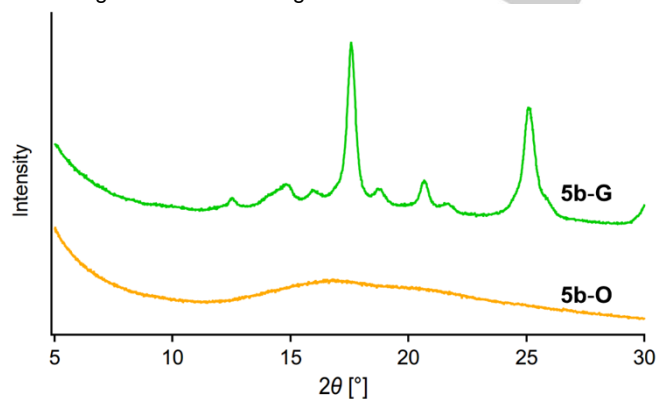


Figure 7. X-ray powder diffraction traces of **5b-G** and **5b-O**.

Conclusion

In conclusion, we succeeded for the first time in the synthesis and evaluation of a TAP bonded system. The construction of this system is based on the repeat of 5-ethynyl-TAP synthesis. The synthesis of 5-ethynyl-TAP consists of the sequential operation of the click reaction of ethynylazidotriflate **2a** with alkynes, cyclization of the resulting triazoles, and elimination of the methoxy group. Further connection of the TAP ring is achieved by applying a sequential operation similar to that of the ethynyl group on the TAP ring. To eliminate the methoxy group, stronger bases were required with the extension of the TAP-connecting system. With the establishment of the synthesis of the 5-ethynyl-TAP ring, various TAP-dimers could be synthesized. Meanwhile, our attempt to synthesize a TAP-trimer afforded only the 2-alkyl derivative **6a**. Comparison of the fluorescence properties between the TAP-monomers, -dimers and -trimer in the diluted solution revealed that the drastic change in fluorescence does not occur by the direct connection of the TAP ring. On the other hand, the TAP bonded system characterized by the linear connection, planar form, and alternating charge showed unique fluorescence properties derived from changes in the aggregation state under the concentrated condition. In particular, TAP-dimer **5b** exhibited mechanochromic fluorescence in the solid state, and we revealed that the mechanical stimulus induced the change from crystalline to amorphous, showing the longer wavelength shift. Furthermore, a novel and interesting fluorescence property was also discovered: additional UV irradiation after grinding leads to a longer wavelength shift and regrinding of the resulting solid causes a shorter wavelength shift, leading back to the state before UV irradiation. Although the synthetic method and interesting fluorescence properties of the TAP-bonded system were first discovered through our research, there are still many fluorescence mechanisms to be elucidated and points to be improved. Further extension of the bonded system, an increase in fluorescence intensity in the solid state, and elucidation of the mechanism underlying the novel fluorescence change between UV irradiation and grinding are the next issues to be examined for TAP bonded systems.

Experimental Section

Decay curves of **5b-G** and **5b-O** with emission lifetimes, computational detail, experimental details, full data, absorption and emission spectra, and ^1H and ^{13}C NMR spectra of each TAP analogs are available in Supporting Information.

Acknowledgements

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Keywords: 1,3a,6a-triazapentalene • TAP-dimer • TAP-trimer • luminescent mechanochromism • TAP-bonded system

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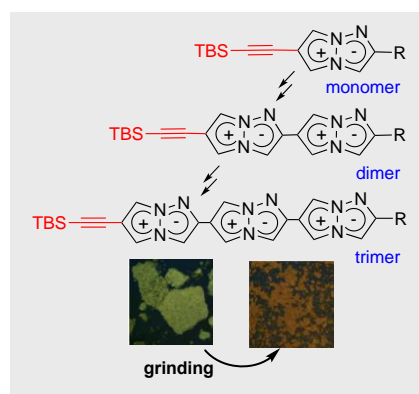
FULL PAPER

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Layout 1:

FULL PAPER

A method of synthesizing a directly connected 1,3a,6a-triazapentalene (TAP) ring system as a linearly bonded aromatic system with a planar form was established. Various TAP-dimers and a 2-alkyl-TAP-trimer were synthesized and their fluorescence properties were evaluated. Some TAP-dimer showed typical mechanochromic fluorescence in the solid state despite their compact molecular size.



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Synthesis and Evaluation of 1,3a,6a-triazapentalene (TAP)-bonded system